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Flow-Induced Liquid Crystalline Solutions Prepared from Aspect Ratio-Controlled Bacterial Cellulose Nanowhiskers

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Cellulose nanowhiskers with the high mechanical strength and aspect ratio have attracted considerable attention as reinforcements in composite materials with nanometric fillers. In this study, aspect ratio-controlled bacterial cellulose nanowhiskers (BCNWs) were prepared simply by varying the hydrolysis time. The nanowhiskers prepared from bacterial cellulose at different hydrolysis times were relatively longer than those produced from cotton and wood cellulose, even after hydrolysis for a long time in a strong acid solution. The bacterial cellulose nanowhiskers did not sediment or flocculate due to the surface acid groups that formed during hydrolysis. This was demonstrated by the phenomenon of flow birefringence. All the samples prepared by hydrolysis for 1–3 hours showed flow birefringence. Lyophilized BCNWs could also be re-dispersed in aqueous solutions, even in polar organic solvents.

Keywords Aspect ratio; bacterial cellulose; microfibril; nanocrystal; whisker

Introduction

Cellulose nanowhiskers (CNWs) are nano-sized, rod-like biomaterials that have attracted considerable interest as reinforcements in composite materials with nanometric fillers owing to their high aspect ratio and mechanical strength [1–9]. They are normally synthesized by a acid hydrolysis treatment because they do not settle or flocculate as a result of the surface acid groups that form during the hydrolysis [10]. Therefore, they have good dispersibility and stability in polar solvents. These non-flocculating charged rod-like CNWs in aqueous suspensions display chiral nematic order above a critical concentration [7,11,16].

CNWs can be obtained from a variety of sources, such as wood [12–15], cotton [1–3], tunicin [4–7], bacteria [16–18] and grass [19]. The length and width of the CNWs can vary according to their source. In the case of cotton and wood, the length is 100–300 nm and the width is 5–20 nm [1–3,12–15]. However, CNWs from tunicin and bacteria are quite long, several micrometers in length with a width of 10–20 nm

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Table 1. Dimensions of the cellulose nanowhiskers from various types of celluloses

Cellulose type	Length (nm)	Width (nm)	Aspect ratio	Hydrolysis condition			Reference
				Acid (wt%)	Temp (°C)	Time (min)	
Cotton	170–350	5–17	15–52	55	60	20	1(a)
				65	70	10	1(b)
				64	45	60	1(c)
Wood	115–300	3–5	20 ~ 30	65	70	10	8(a)
				65	72	35	1(b)
				65	72	35	8(c)
Tunicate	100<	10–20	–	50 (V/V)	30	Overnight	2(b)
				75	60	90	2(d)
Bacterial	100<	5–50	–	65	70	30	9(a)
				60	51	60	9(c)

[4–7,16–18]. Because tunicin and bacterial cellulose have relatively high crystallinity, there is less non-crystalline region to remove by acid hydrolysis than with cotton and wood cellulose [26]. Therefore, their aspect ratio is relatively high. Table 1 shows the properties and hydrolysis conditions of the CNWs produced from various types of celluloses. The main factors affecting cellulose hydrolysis are the acid concentration, hydrolysis temperature and time. The results suggest that cellulose hydrolysis occurs through the co-effects of a range of factors.

Bacterial cellulose is a sustainable natural polymer belonging to the polysaccharide family, and is produced by acetic bacteria, e.g., *Acetobacter xylinum*. This bacterial cellulose has a unique structure and properties in terms of its purity, high crystallinity and high mechanical strength [16–18]. The typical structure of cellulose produced by *Acetobacter xylinum* is a twisting ribbon form composed of subfibrils [20,21]. This twisting ribbon form is produced in several steps. In the first step, the terminal complexes are arranged linearly and the glucan chain aggregates consisting of approximately 6–8 chains are elongated from the complex. In the second step, these subfibrils are assembled to form microfibrils, which are followed by their tight assembly to form a ribbon as the third step. This ribbon forms with high crystallinity, which imparts high mechanical strength and a high aspect ratio to these bacterial cellulose nanowhiskers. In this study, bacterial cellulose nanowhiskers (BCNWs) were prepared at different hydrolysis times. The aim was to produce aspect ratio-controlled bacterial cellulose nanowhiskers with all nematic phase separation within a narrow concentration range.

Experimental Section

Materials

Gluconacetobacter xylinum BRC-5 was cultured on Hestrin and Schramm (HS) medium consisting of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. The cells precultured in a test tube for 7 days were inoculated into a 500 mL Erlenmeyer flask containing 100 mL of HS medium. The cells in the flasks were

incubated statically at 30°C for 14 days. The fabricated cellulose pellicles were purified by immersing in 0.25 M aqueous sodium hydroxide solution for 48 h at room temperature in order to eliminate the cells and components in the culture liquid. Then the bacterial cellulose pellicles were neutralized by repeated washing with distilled water. The purified cellulose pellicles were stored in distilled water at 4°C to prevent drying. H_2SO_4 (DC Chemical Co. Ltd., Korea, 95%) was used to produce the BCNWs.

Preparation of Bacterial Cellulose Nano-Whisker (BCNW)

The purified bacterial cellulose pellicles were disintegrated using a homogenizer, washed thoroughly with deionized water by filtration and then lyophilized. The lyophilized bacterial cellulose fragments were mixed with 65 wt% sulfuric acid and stirred continuously at 70°C for $1 \sim 3$ h. The resulting BCNWs were collected and purified by repeated centrifugation (9500 rpm, 30 min) and dialysis for 7 days. The BCNWs solution was then sonicated for one hour at ambient temperature using an ultrasonic generator (Kyungill Ultrasonic Co., Korea) with a nominal frequency of 28 kHz and a power of 600 W.

Dispersibility Test

The dispersion of the BCNWs in aqueous solution was investigated by an inspection of the birefringence between two crossed polarizers without a further ultrasonic treatment. Lyophilized bacterial cellulose nanowhiskers were then transferred to a 30 mL glass vial, and deionized water and tetrahydrofuran were added in succession. The bacterial cellulose nanowhisker solutions (1 mg/ml) were then sonicated for several minutes. (In the case of tetrahydrofuran, the ultrasonic treatment was applied for 1 hour) The dispersion was assessed by examining the dispersion between the two crossed polarizers.

Characterization

The size and shape of the bacterial cellulose nanowhiskers were examined by transmission electron microscopy (TEM, CM200, Philips, USA). One drop of a diluted suspension of bacterial cellulose nanowhiskers was placed onto a carbon coated grid and stained by placing one drop of a 2 wt% solution of uranyl acetate onto a carbon coated grid directly. The morphology and sulfur content of the lyophilized BCNWs were observed by scanning electron microscopy (SEM, S-4300 with EDS KEVEX, Hitachi, Japan) at an accelerating voltage of 15 kV after precoating the sample with a homogenous Pt layer by ion sputtering (E-1030, Hitachi, Japan).

Results and Discussion

Cellulose nanowhiskers can be produced using different temperatures, times and sulfuric acid concentrations. In the case of hydrolysis in sulfuric acid, the acid concentrations range from 30–65 wt% and the temperature varies from ambient temperature to 80°C. It is difficult to prepare aspect ratio controlled cellulose nanowhiskers using literature methods, and many experiments will be needed to optimize the conditions. In this study, aspect ratio-controlled bacterial cellulose nanowhiskers

Table 2. Reaction conditions of the bacterial nanowhiskers

Sample	H_2SO_4 solution concentration (wt%)	Temperature (°C)	Volume of BC/solution (g/ml)	Time (h)
BCNW1 h	65	70	0.1/100	1
BCNW2 h	65	70	0.1/100	2
BCNW3 h	65	70	0.1/100	3

were prepared by varying the hydrolysis time. A reaction too long will digest the cellulose completely to yield its component sugar molecules, and a reaction too short will yield only large fibers and aggregates. Table 2 shows the applied reaction conditions. Under these conditions, the hydrolysis of bacterial cellulose was only affected by the applied time. Figure 1 shows bacterial cellulose nanowhiskers that were prepared after 1–3 hours hydrolysis. The BCNW1 h has a long length of $1 \sim 2\,\mu m$ and a width of 30 nm, i.e., an aspect ratio >40. These high aspect ratio-bacterial cellulose nanowhiskers are similar to those reported elsewhere [16–18]. In the case of BCNW2 h and BCNW3 h, which were hydrolyzed for 2 and 3 h, respectively, the lengths were reduced to approximately 800 nm and 500 nm, respectively. However, their widths were similar. Therefore, their aspect ratio was reduced. Figure 2 shows the length distribution of all samples. The prepared BCNWs showed a wide range of lengths and standard deviations but their length decreased significantly with increasing hydrolysis time. In this study, the nanowhiskers prepared from bacterial cellulose were relatively longer than cotton and wood cellulose, even after hydrolysis for 3 hours, on account of its higher crystallinity and ribbon shaped crystalline structure. Since these ribbon shaped crystalline bundles cannot be penetrated by acid and water molecules, they are hydrolyzed by a surface reaction process [22]. Therefore, the hydrolysis rate of the ribbon shaped crystalline bundles was relatively slow and the aspect ratio of the BCNWs could be controlled by the hydrolysis time. Electrostatic repulsion is achieved by sulfuric acid hydrolysis, which introduces negatively charged sulfate groups to the whisker surface through esterification [23]. The surface charge was measured as a function of the sulfur content. The sulfur content of the BCNWs increased with increasing reaction time, which is consistent with previous reports [24,25]. Table 3 shows the information of BCNWs prepared from different hydrolysis conditions. Because of the negatively charged sulfate moiety, the formation of hydrogen bonding between the individual whiskers was limited and the dispersion was stable in an aqueous solution [26]. Therefore, none of the samples settled or flocculated after a long period. A dispersion of individual whiskers

Table 3. Properties of the cellulose nanowhiskers prepared by controlling the hydrolysis time for 1–3 h

	BCNW1 h	BCNW2 h	BCNW3 h
Average length (nm)	1380	840	540
Average width (nm)	30	30	30
Aspect ratio	46	28	18
Standard deviation (nm)	470	390	330
Sulfur contents (wt%)	0.99	1.57	1.99

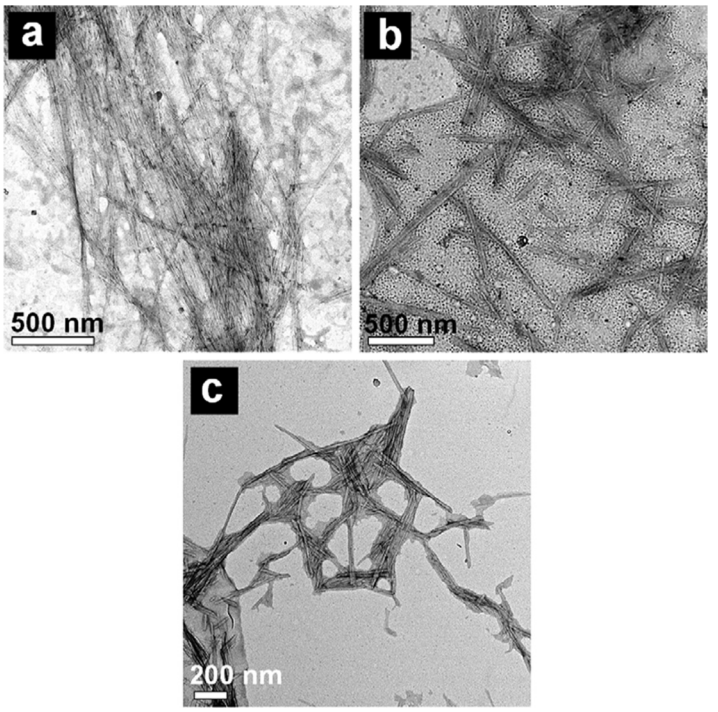


Figure 1. TEM image of BCNW1 h (a), BCNW2 h (b) and BCNW3 h (c) prepared by controlling the hydrolysis time for 1–3 h.

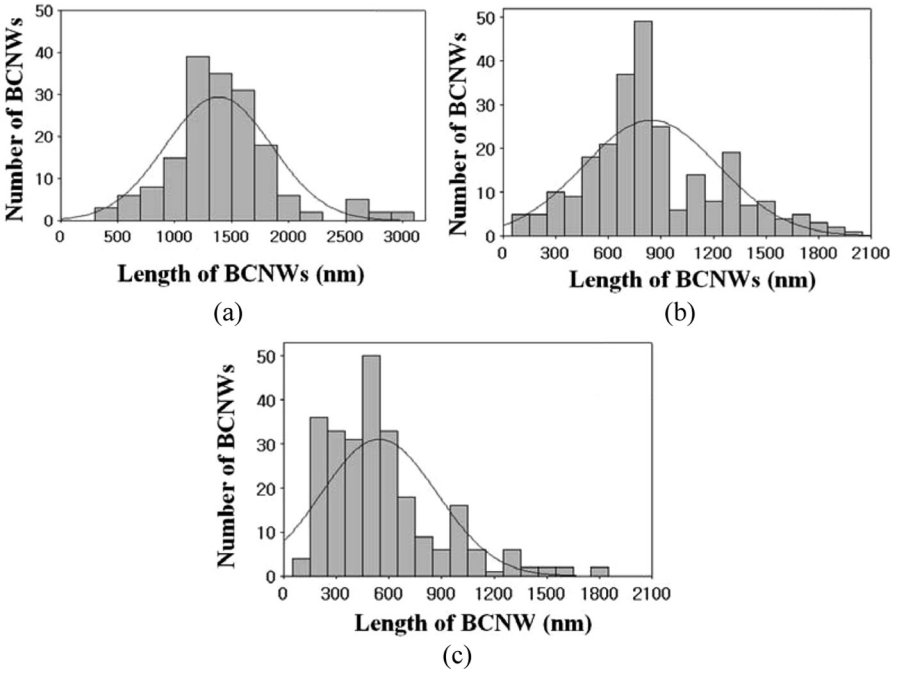


Figure 2. Length distribution of BCNW1 h (a), BCNW2 h (b) and BCNW3 h (c).

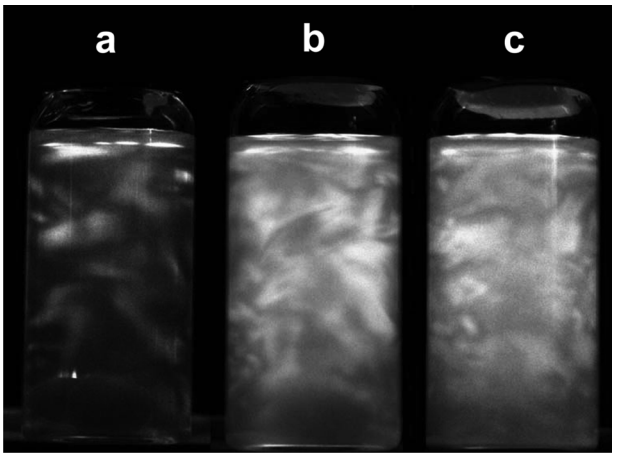
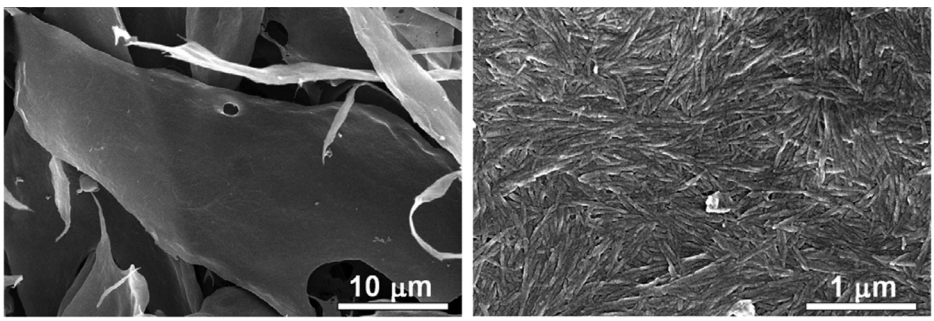


Figure 3. Photographs of the dispersions of BCNW1 h (a), BCNW2 h (b) and BCNW3 h (c) in water, viewed through crossed polarizers.

can be demonstrated by the phenomenon of flow birefringence [27]. The BCNWs were well separated and showed flow birefringence, as shown in Figure 3. In this study, all samples showed flow birefringence suggesting that they contained a large number of single BCNWs. The BCNWs were lyophilized to investigate the redispersibility of the BCNWs in an aqueous solution. During the freeze-drying process, the BCNWs tended to aggregate and their morphology appeared to be flake-shaped with rigid aggregation as shown Figures 4 (a), (b). However, lyophilized BCNWs were easily re-dispersed in aqueous solutions because of the surface acid groups that formed during the acid hydrolysis [10]. Once ultrasound was applied to the BCNWs, they re-dispersed within several minutes and exhibited flow birefringence, as shown in Figures 5 (a)–(c). The BCNWs could be dispersed in polar organic solvents, such as tetrahydrofuran. Figure 5 (d) shows the flow birefringence of the BCNWs in tetrahydrofuran. This suggests that the BCNWs have potential in a range of reinforcement fields. In particular, BCNWs with a large aspect ratio will be good reinforcements because of the good mechanical properties and thermal stability of bacterial cellulose. Further research into polymer nanocomposites is currently underway.



(a) (b)

Figure 4. SEM image of the lyophilized bacterial cellulose nanowhiskers.

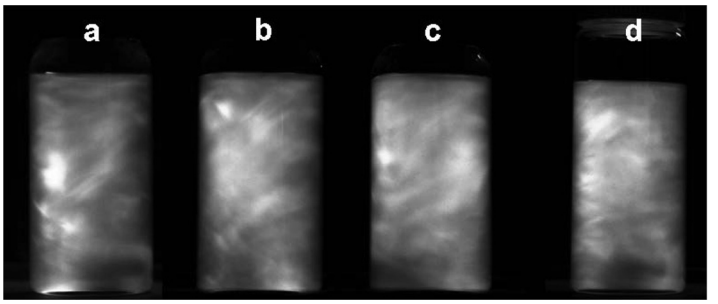


Figure 5. Photographs of the re-dispersions of lyophilized BCNW1 h (a), BCNW2 h (b), BCNW3 h (c) in water and re-dispersions of lyophilized BCNW1 h (d) in tetrahydrofuran, viewed at 1 mg/ml through crossed polarizers.

Conclusion

In this study, aspect ratio-controlled bacterial cellulose nanowhiskers were prepared at various hydrolysis times. BCNW1 h had a long length of $1 \sim 2\,\mu m$, a width of 30 nm and relatively high sulfur content compared to BCNW2 h and BCNW3 h. The nanowhiskers prepared from bacterial cellulose had longer lengths than those made from cotton and wood cellulose, even after hydrolysis for 3 hours. None of the samples settled or flocculated after long periods because of the negatively charged sulfate moiety incorporated on the surface of the BCNWs during hydrolysis. A dispersion of individual whiskers was demonstrated by the phenomenon of flow birefringence. All the samples showed flow birefringence. Lyophilized BCNWs were also redispersed in an aqueous solution, even in polar organic solvents. This suggests that BCNWs have potential applications in a variety of reinforcement fields.

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